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Abstract:

A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

Brent D. Viers, PRSM, Air Force Research Laboratory, 10 Saturn Blvd., Edwards AFB, CA 93524, Timothy S. Haddad, ERC and Air Force Research Laboratory, Edwards AFB, CA 93524, and Michael T. Bowers, Chemistry, U.C. Santa Barbara, Santa Barbara, CA 93106.

Polyhedral Oligomeric Silsesquioxanes (POSS) are of interest because the hydrolysis and condensation of the silane precursors can be controlled to form incompletely condensed "scaffolds" which can then be functionalized (via condensation) with differing moieties. However, conventional wisdom held that isolation of ionized scaffolds was impossible due to the increased reactivity of the ionic siloxy fragments. However, recent results have shown that certain POSS based salts are indeed stable. This talk will review the progress in formation of ionic species, and the potential of these intermediates for "rational synthesis" of other nanostructures.

FILE

MEMORANDUM FOR PRS (In-House/Contractor Publication)

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-~~049~~ 053**
Brent D. Viers (AFRL/PRSM); Timothy Haddad (ERC); Capt. Rene I. Gonzalez (AFRL/PRSM),
"~~Structure and Modeling of POSS Monomers~~" "A Reanalysis of POSS Ions & Salts"

Viers
5416

American Chemical Society Conference **(Statement A)**
(New Orleans, LA, 23-27 Mar 2003) (Deadline: 27 Feb 2003 – PAST DUE)

A reanalysis of polyhedral oligomeric silsesquioxane ions and salts

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Erin Baker, Jennifer Gidden, Michael Bowers, †Stan Anderson

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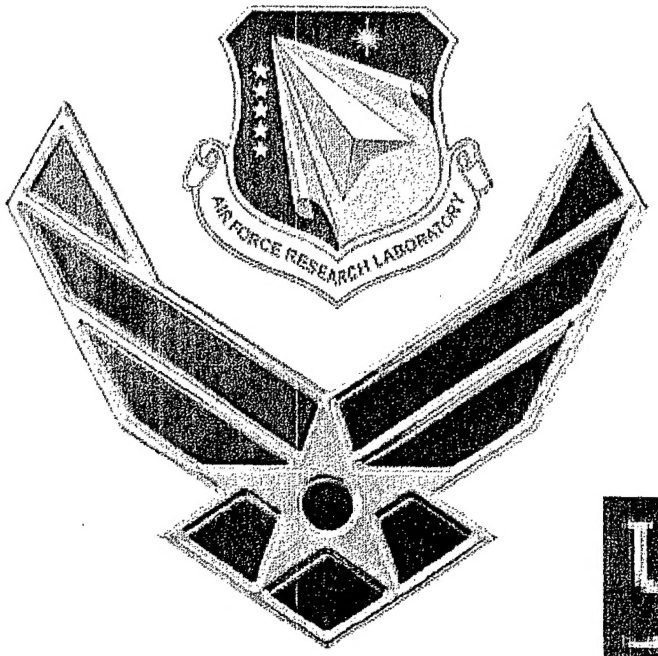
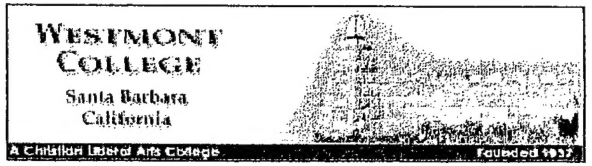


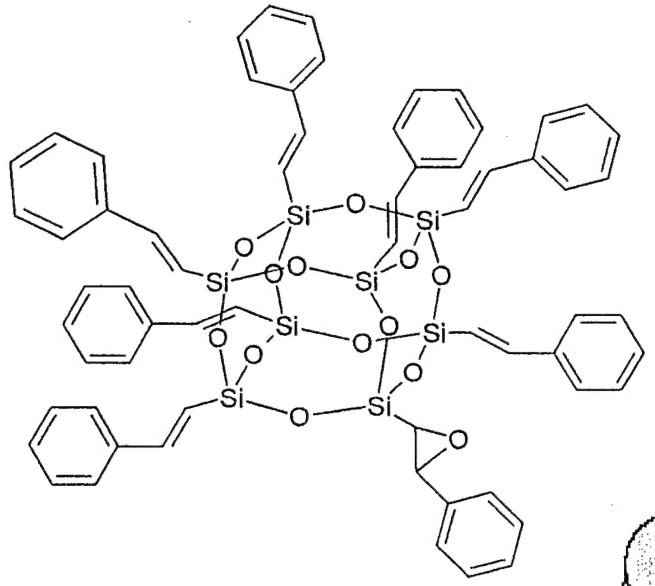


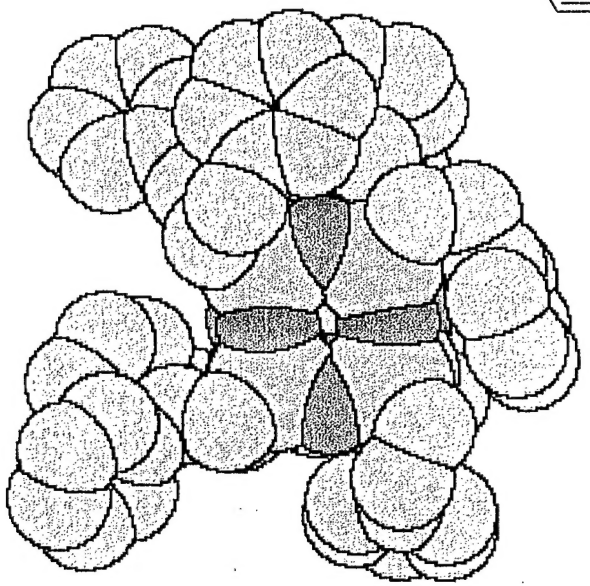
Commercial Success

POSS incorporation leads to reduced shrinkage upon cure?

File name

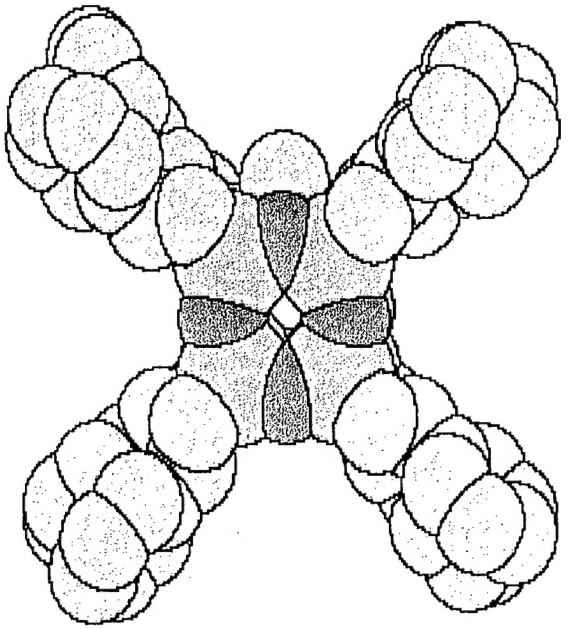
POSSible Structures





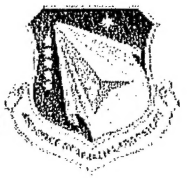
$Na^{+}PhenEt_8T_8$

Epoxy POSS Intermediate in Size?



$Na^{+}Sty_8T_8$

Application Of Ion Mobility Measurements



Ion Mobility → Collision Cross-Sections ← Molecular Modeling

Collision Cross-Sections → 3-D Structural Information

3-D Structural Information →

- Identify Mixture Distributions
- Structural differences with different "R" groups
- Structures of Intermediates
- "impurities" in synthesis
- How structure changes with size (POSS oligomers)
- How POSS attaches to polymers

Modifications needed for POSS Modeling

- New parameters for all Si bonds, angles, dihedrals, and torsions (adapted from Si and Si-X parameters obtained from polysiloxane work).

  Ref: H.Sun and D. Rigby, *Spectrochimica Acta A*, 1997, *53*, 1301.

- Atom charges obtained from Gaussian calculations on model systems and x-ray structures; adjusted using AMBER RESP protocol.

- Starting structures built in Hyperchem and imported into AMBER.

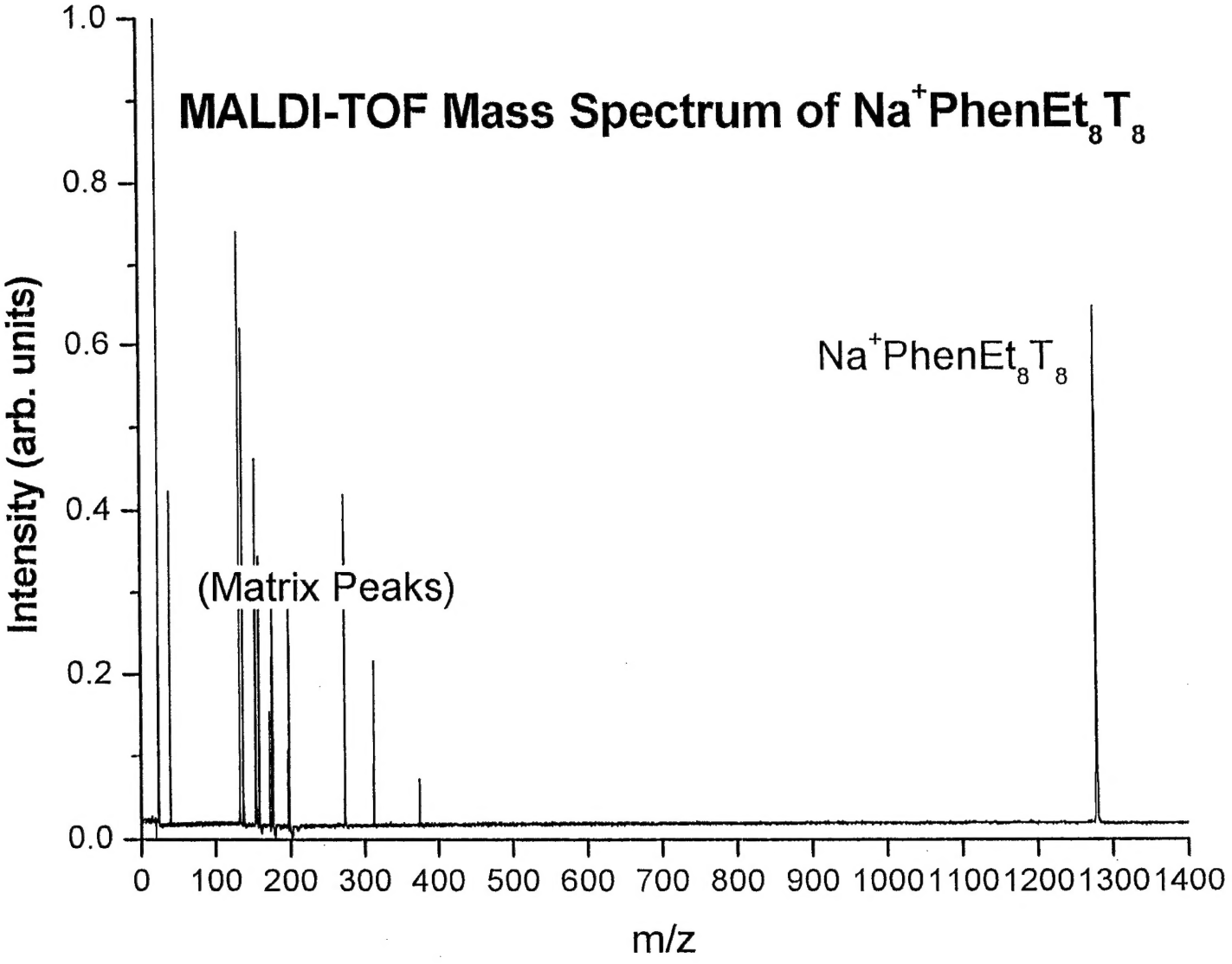
Comparison of Sizes: $PhenEt_8T_8$ to Sty_8T_8

	x-ray	ESI	MALDI	Theory
$Na^+Sty_8T_8$	341	339	346 [a)]	338
$Na^+PhenEt_8T_8$			267	265 [b)]

a) most abundant peak

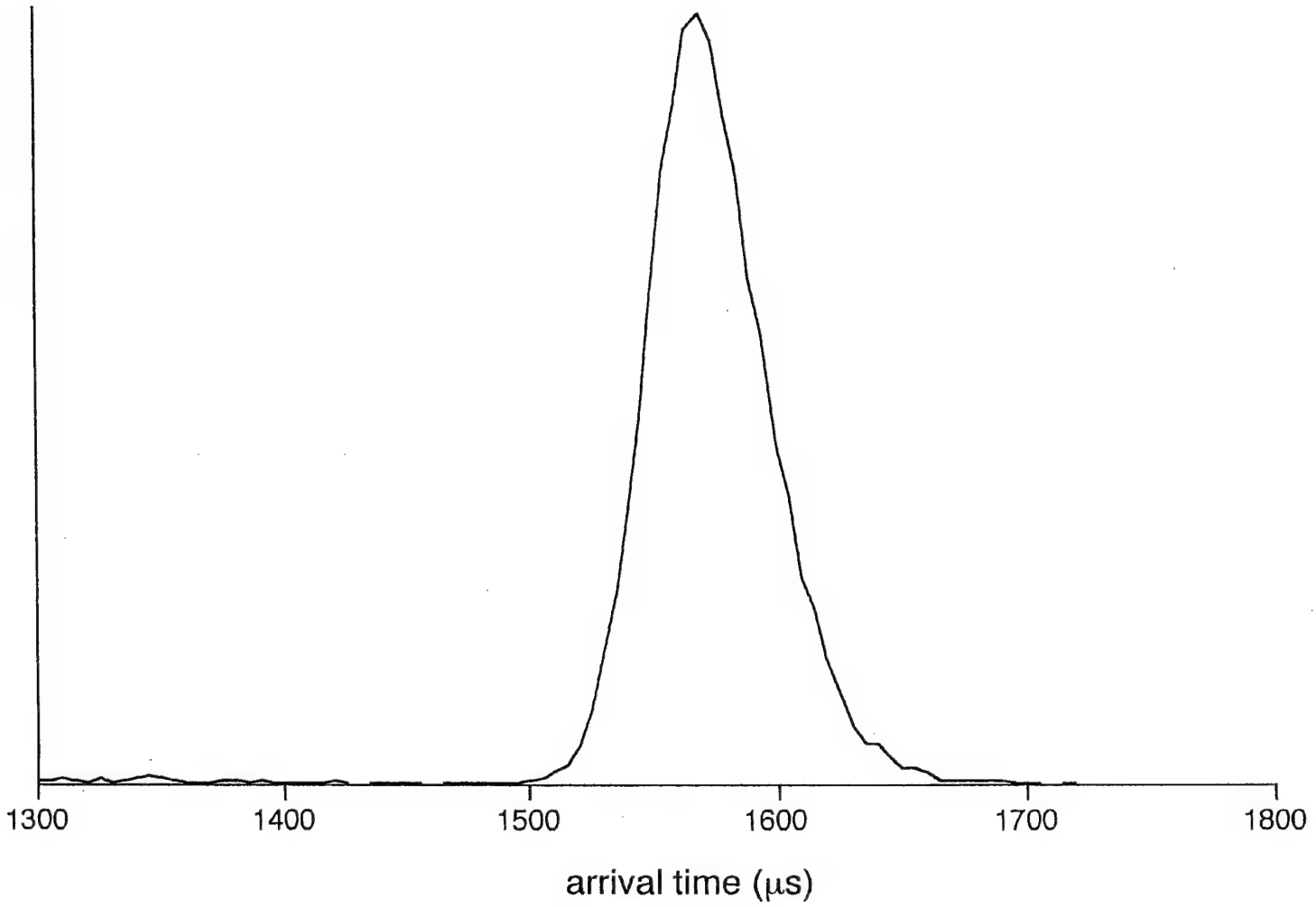
b) from scatter plot – average value of lowest 7 kcal/mol structures

MALDI TOF of $Na^+PhenEt_8T_8$



File name

$Na^+PhenEt_8T_8$ ATD



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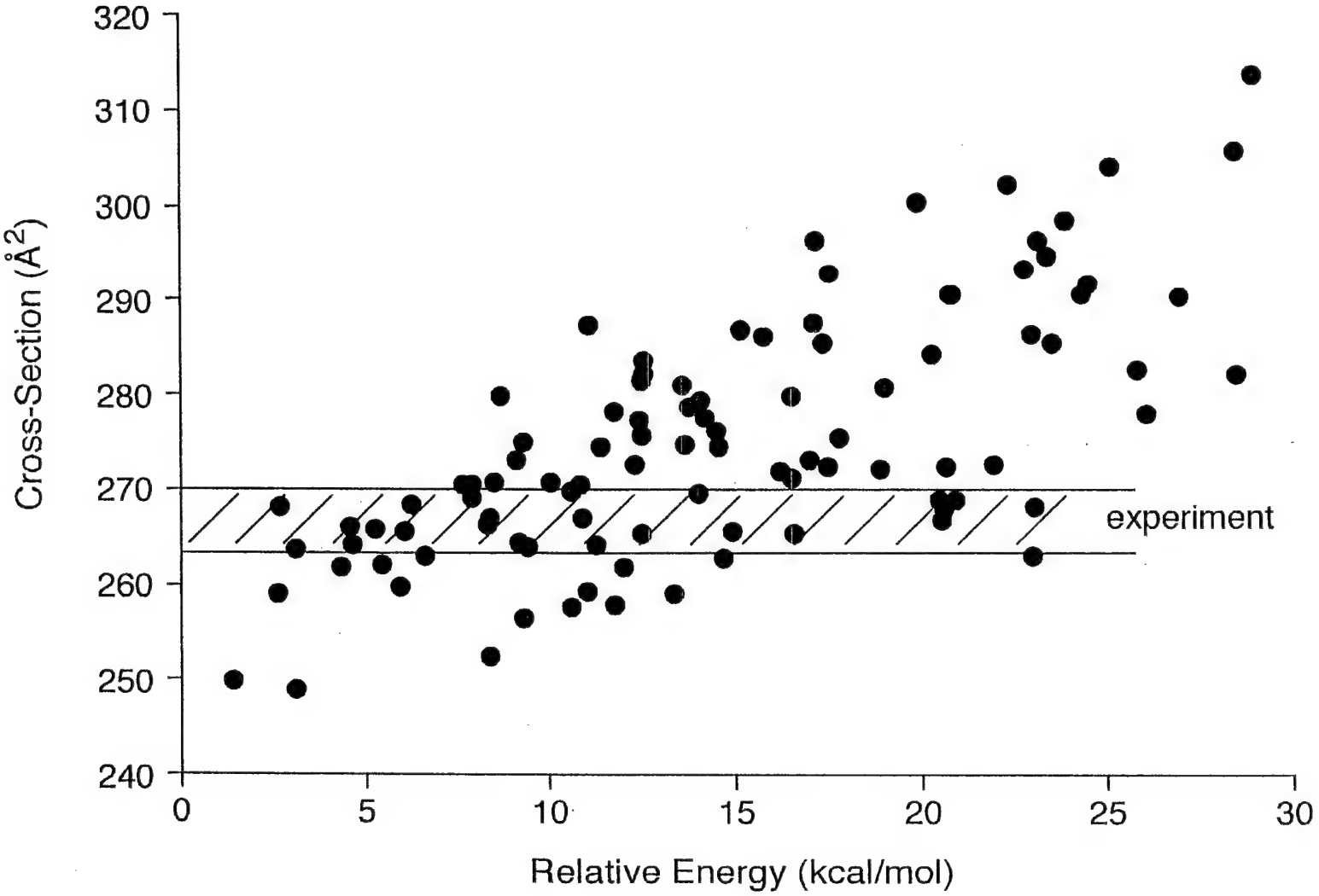
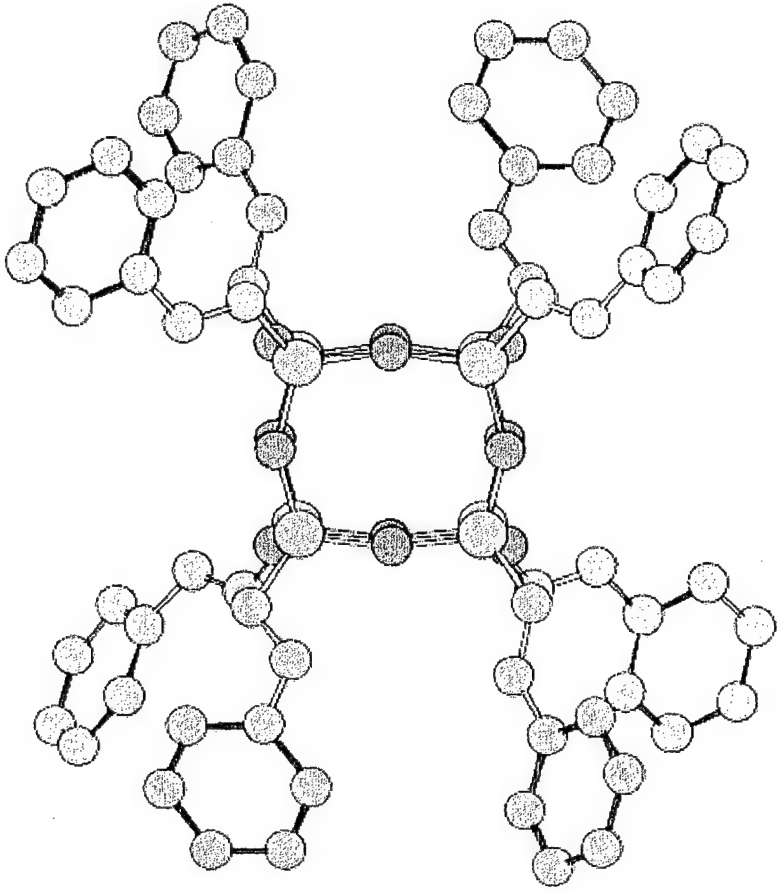
Energetic Calculations

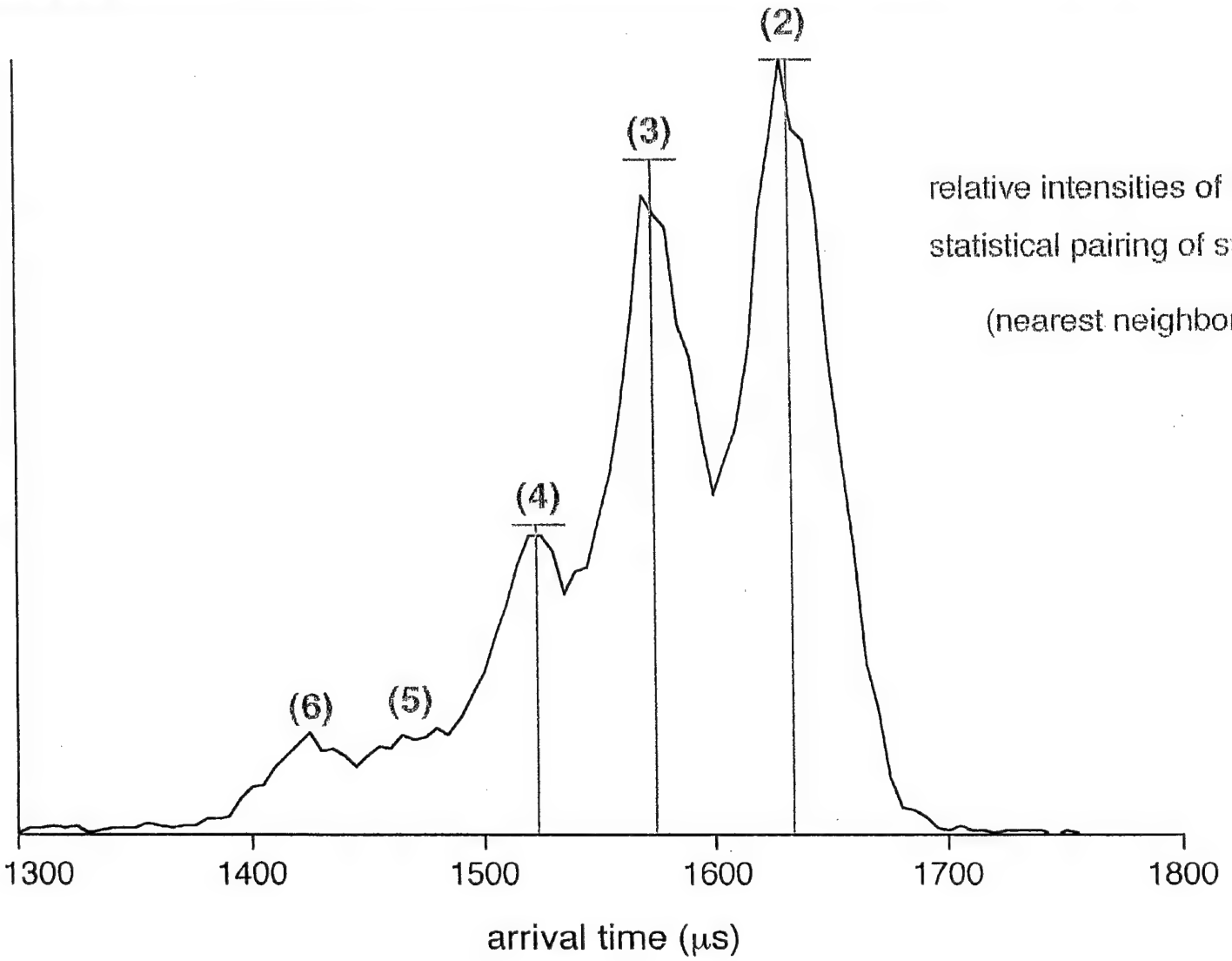


File name

X-ray Structure of Sty_8T_8



MALDI TOF of $Na^+Sty_8T_8$

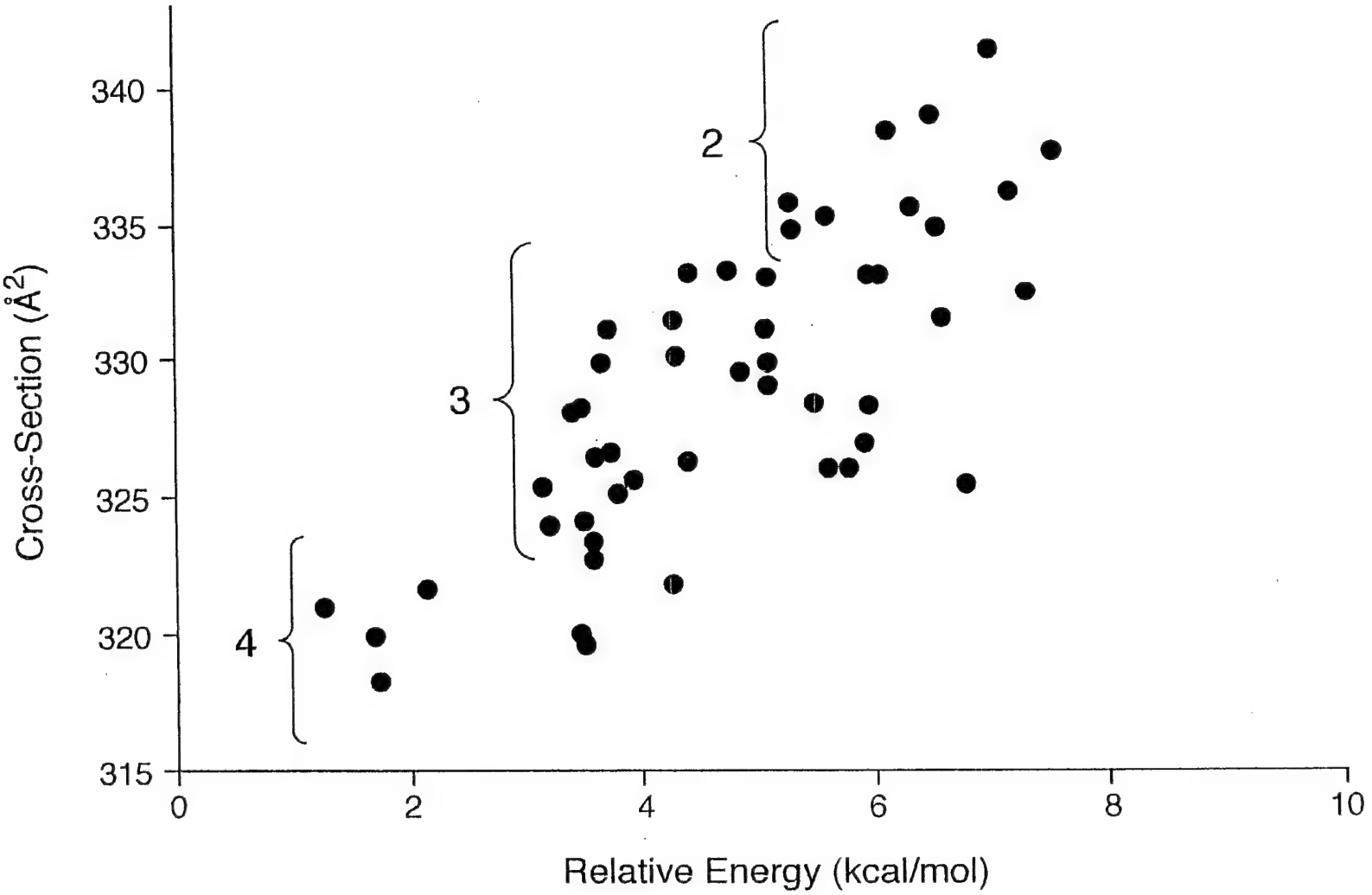


relative intensities of peaks follow statistical pairing of styrenes

(nearest neighbors only)

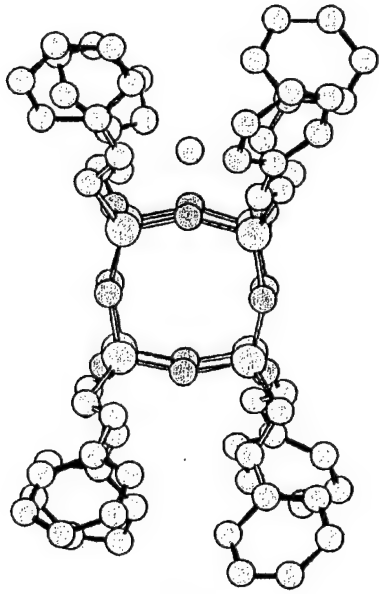
File name

Energetic Calculations



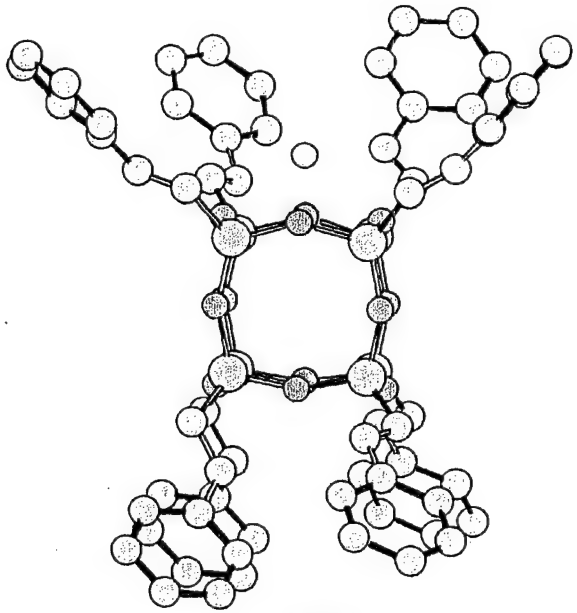
File name

Calculated $Na^+Sty_8T_8$ Structures



(4)
320 Å^2

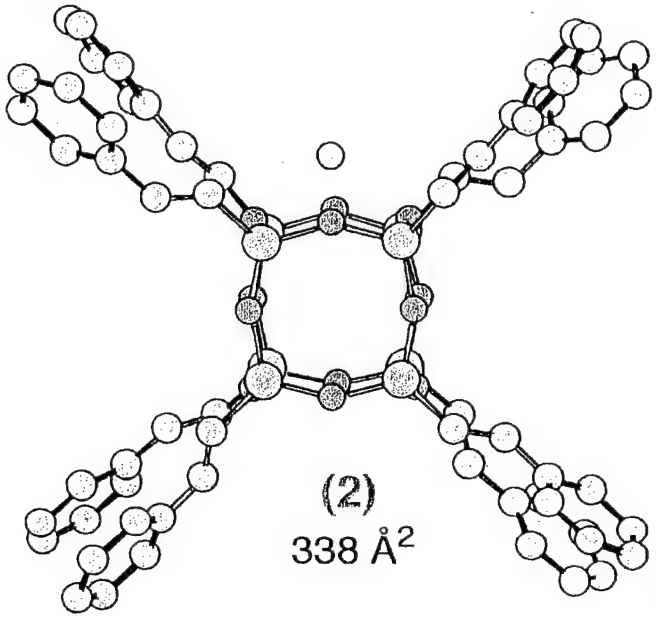
4 pair



(3)
328 Å^2

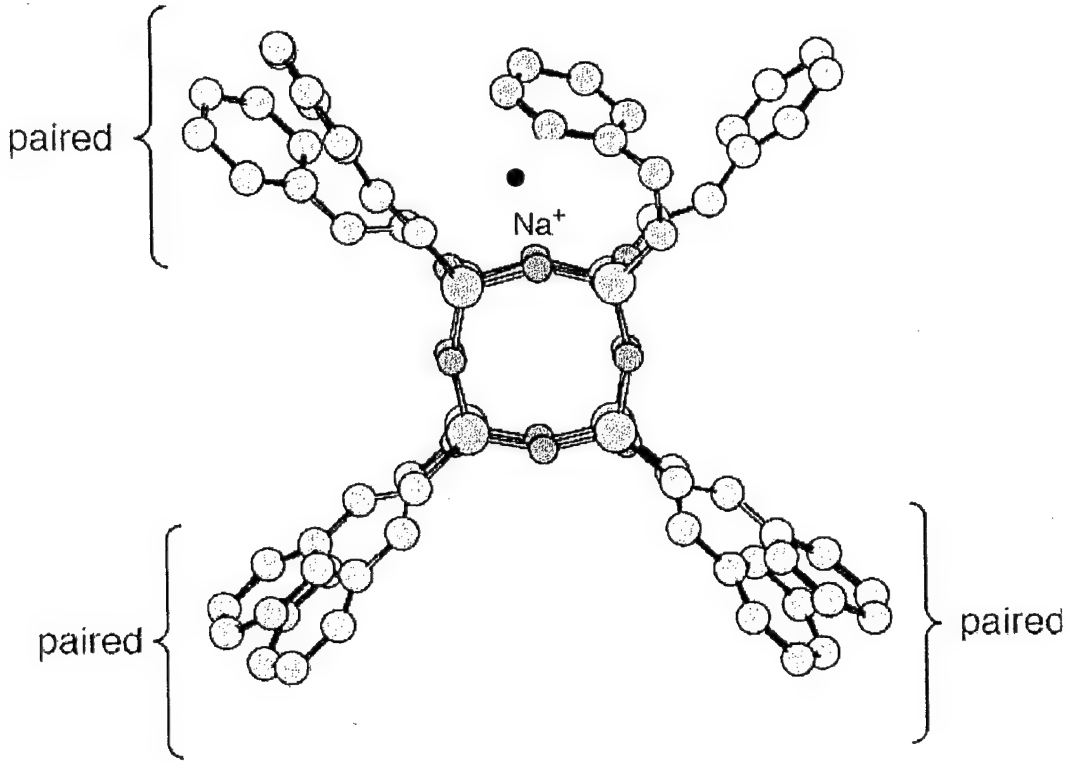
3 pair

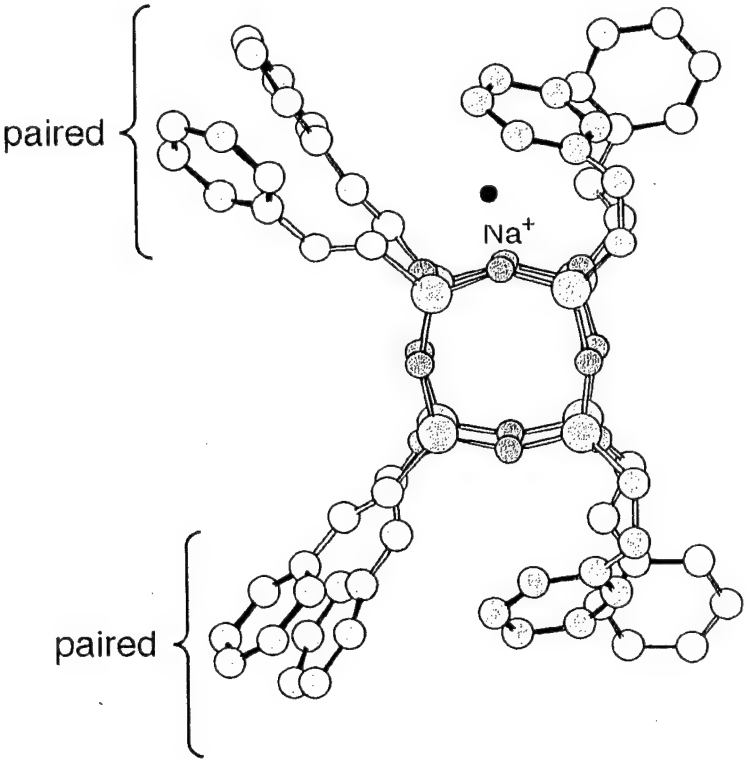
2 pair



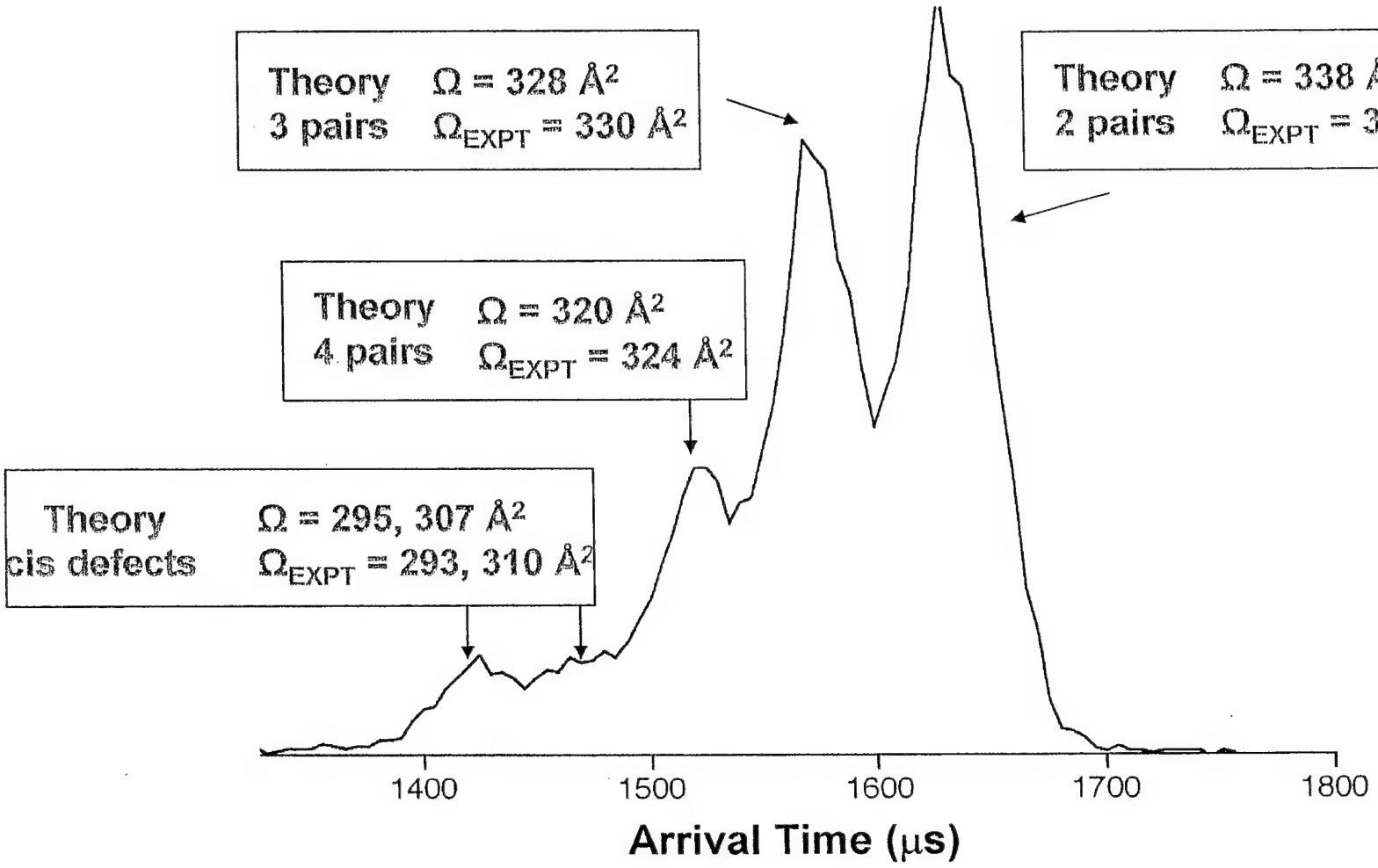
(2)
338 Å^2

Sty_8T_8 Cis Defect Structures





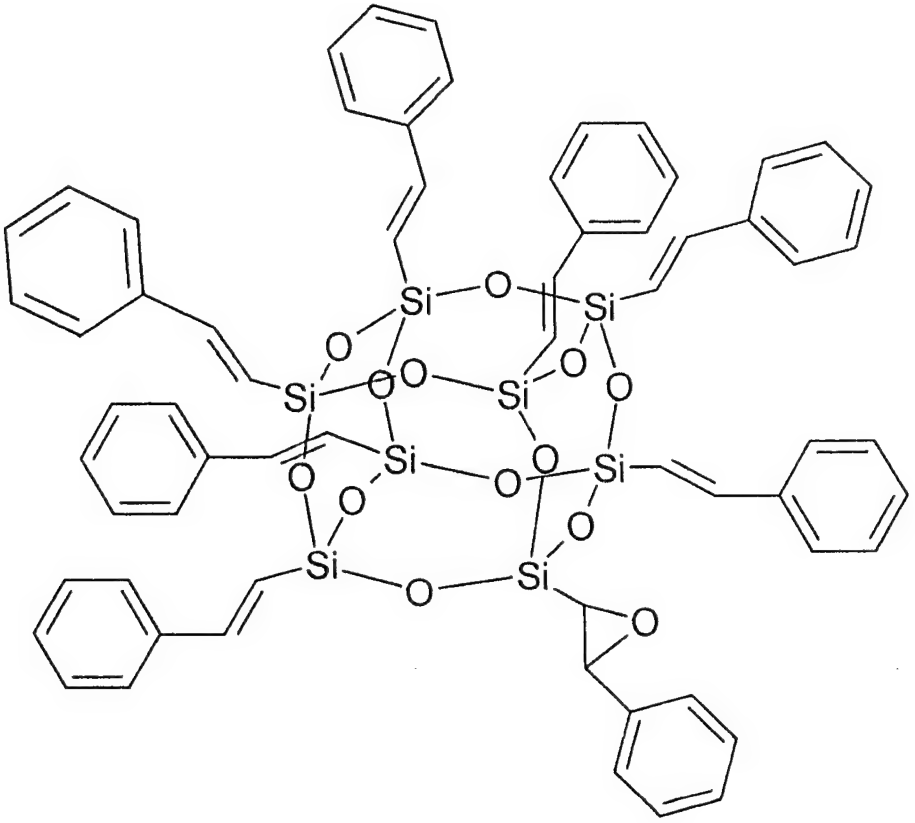
Comparison of Theoretical and Experimental Cross-sections



Summary for Sty_8T_8

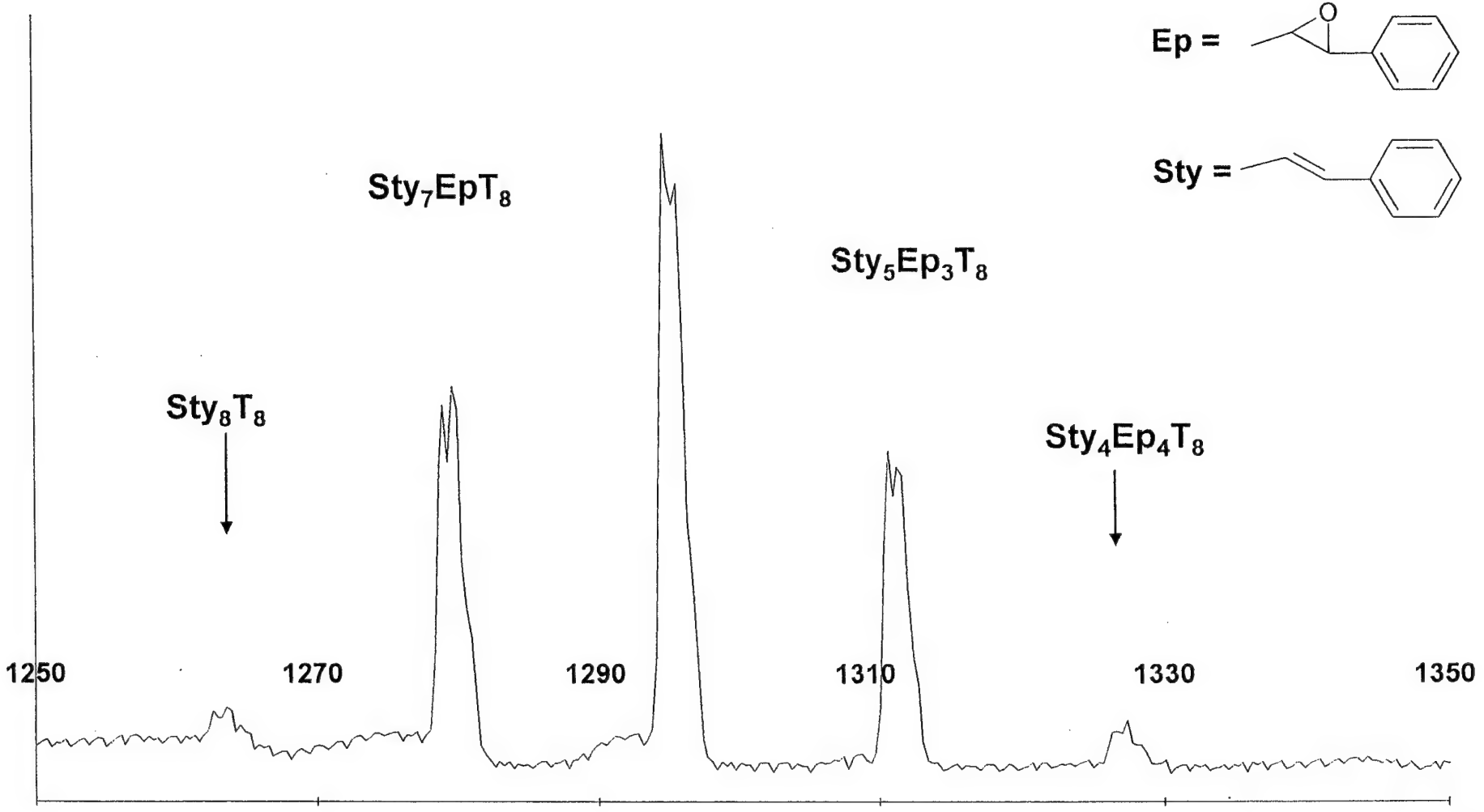
- Most compact structure (lowest σ) is the most stable
- Least compact structures are most abundant
- Quantitative agreement of experimental and theoretical σ's
- MALDI intensities in semi-quantitative agreement with statistical pairing of phenyl groups
- X-ray structure quantitatively agrees with least compact structure

Sty_7EpT_8

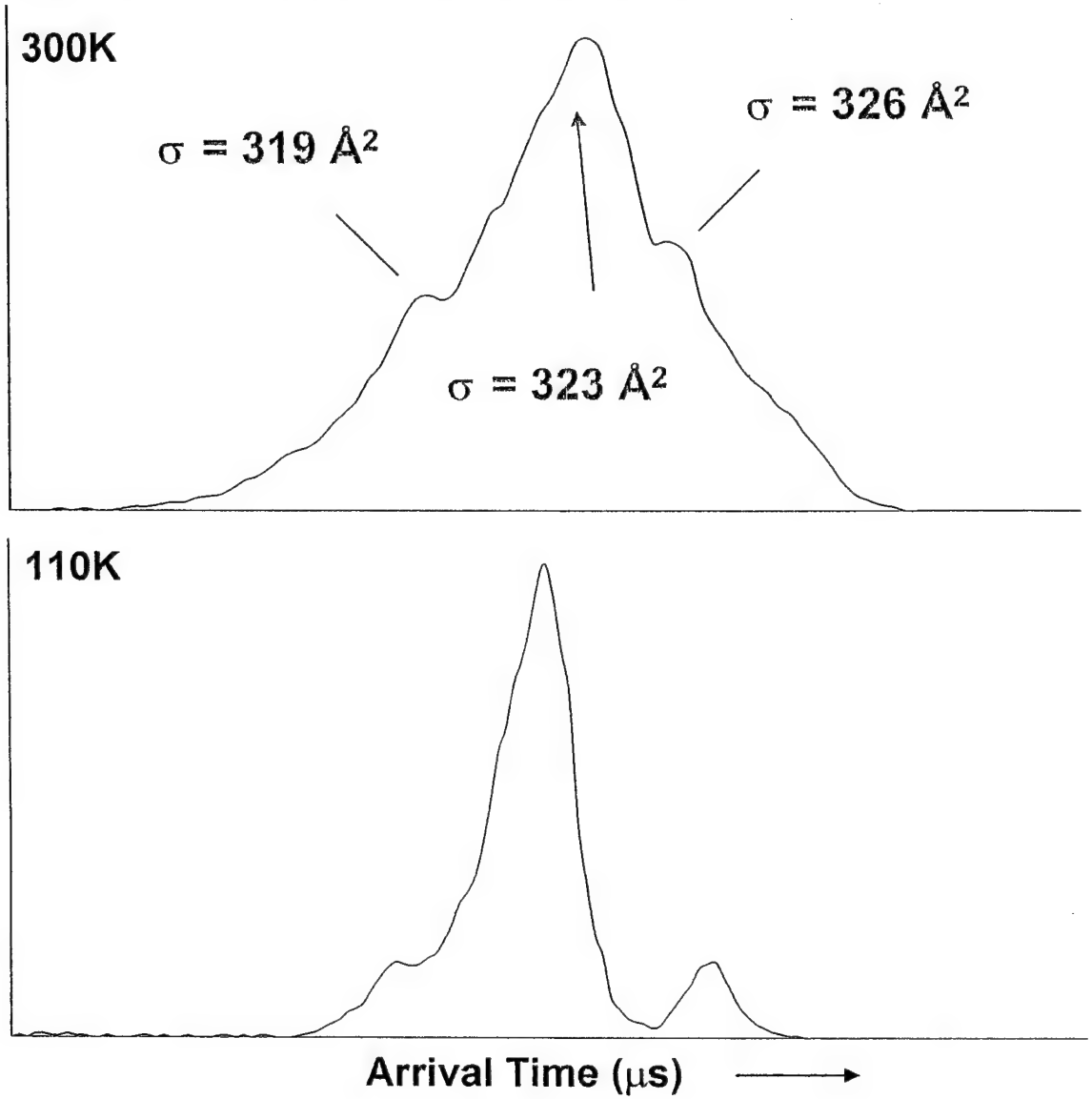


File name

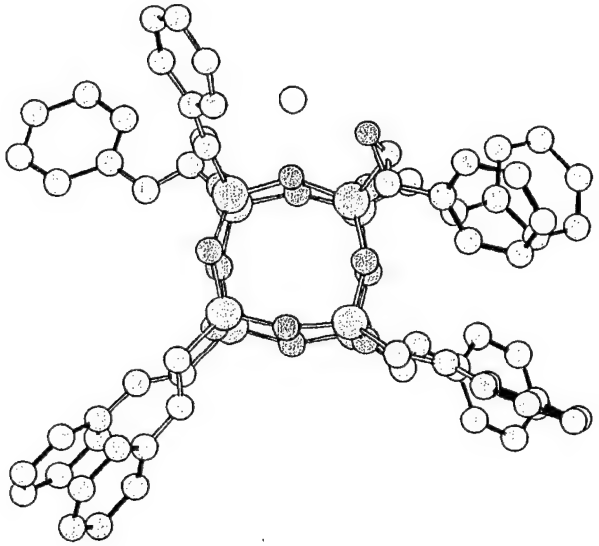
Styrene Epoxy T_8 POSS System Mass Spectrum



$Na^+Sty_7EpT_8$ ATDs



$Na^+Sty_7EpT_8$ Theoretical Structures

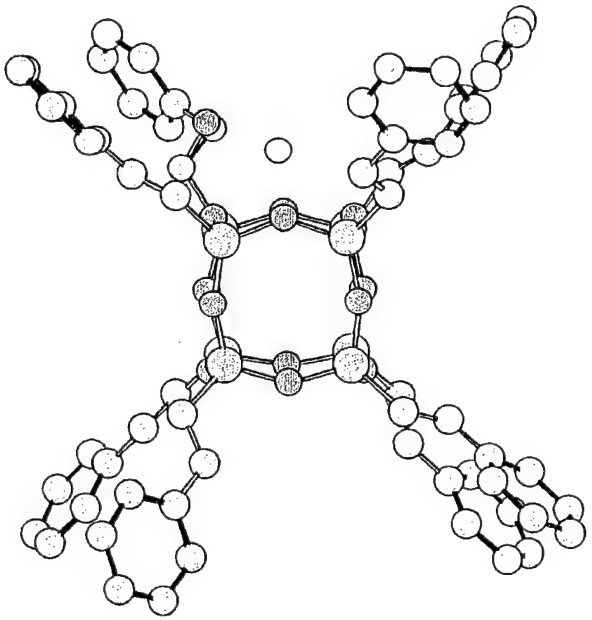


2 Pairs

σ_{Theory} = 320 Å^2

σ_{EXPT} = 319 Å^2

~13%

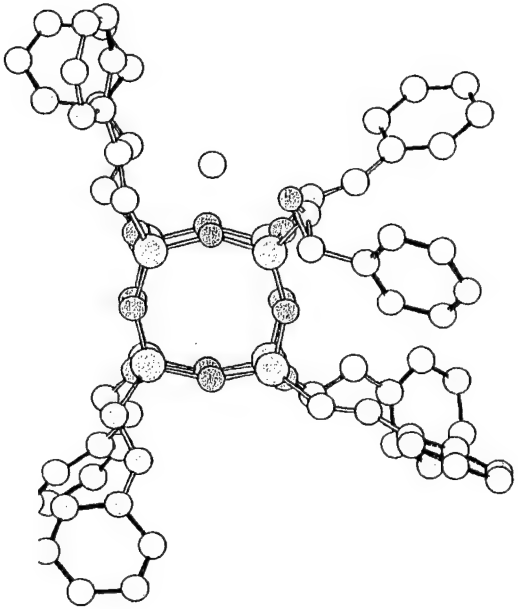


No Pairs

σ_{Theory} = 328 Å^2

σ_{EXPT} = 326 Å^2

~13%



1 Pair

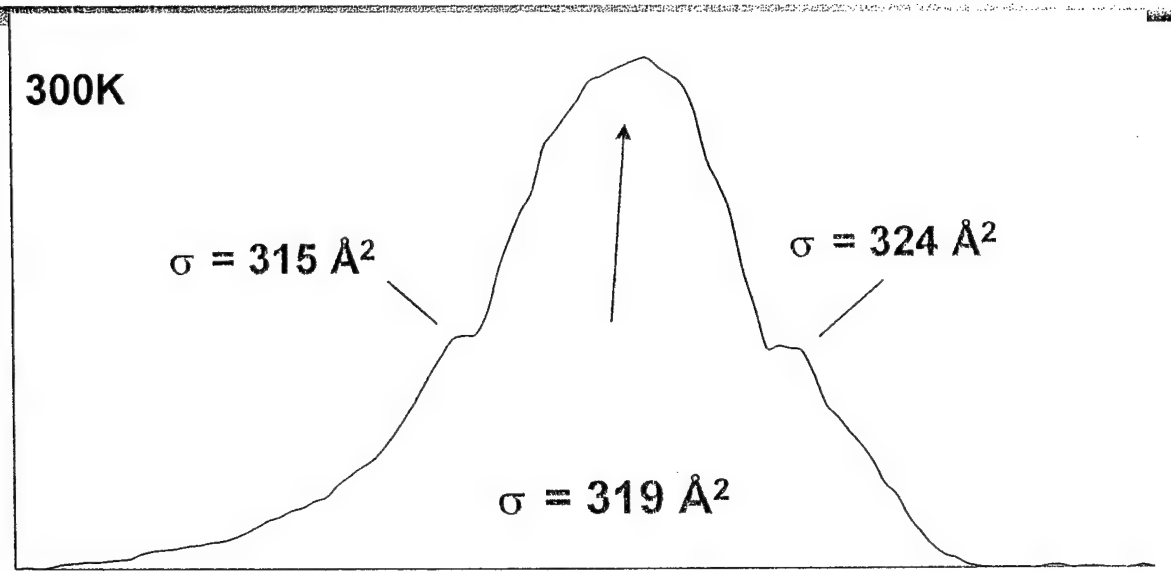
σ_{Theory} = 324 Å^2

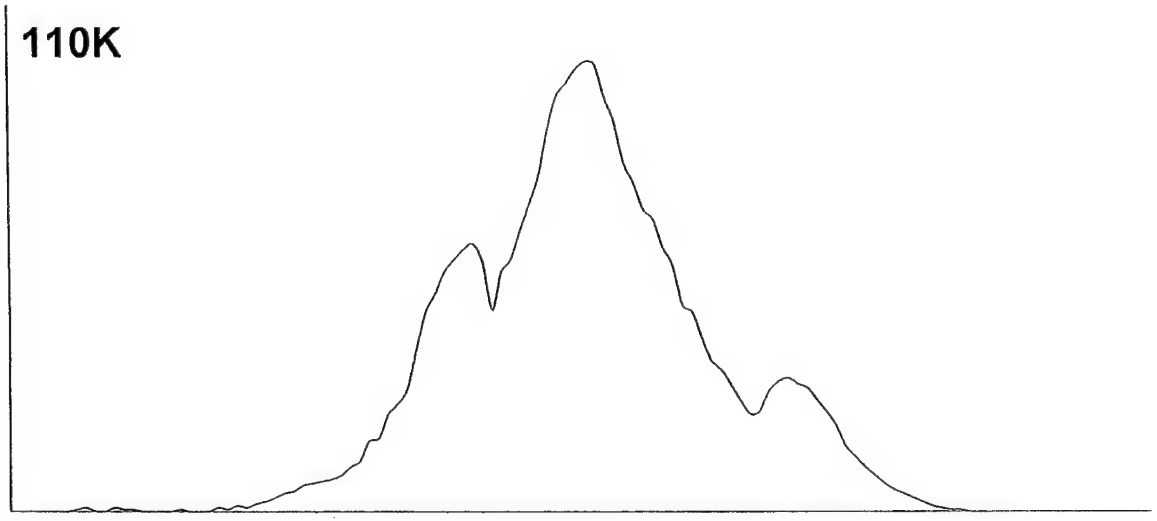
σ_{EXPT} = 323 Å^2

~74%

File name

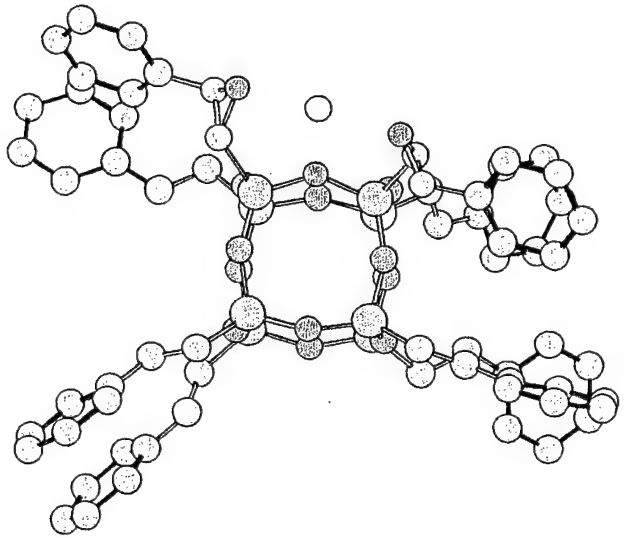
$Na^+Sty_6Ep_2T_8$ ATDs





Arrival Time (μs) ⟶

$Na^{+}Sty_6Ep_2T_8$ Theoretical Structures

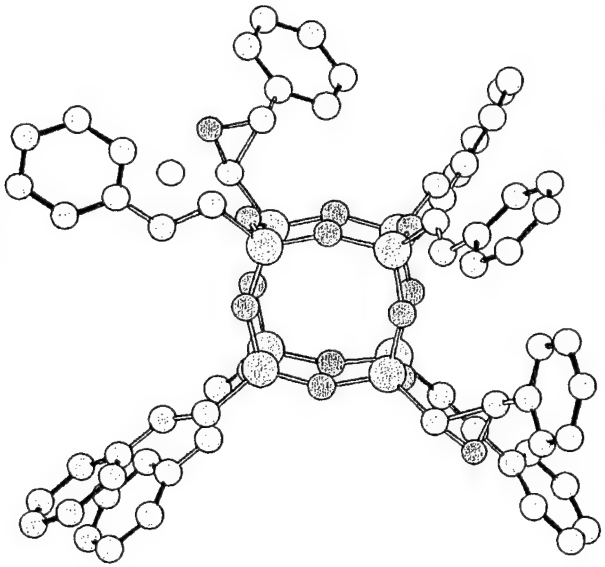


edge

σ_{Theory} = 314 Å^2

σ_{EXPT} = 315 Å^2

~22%

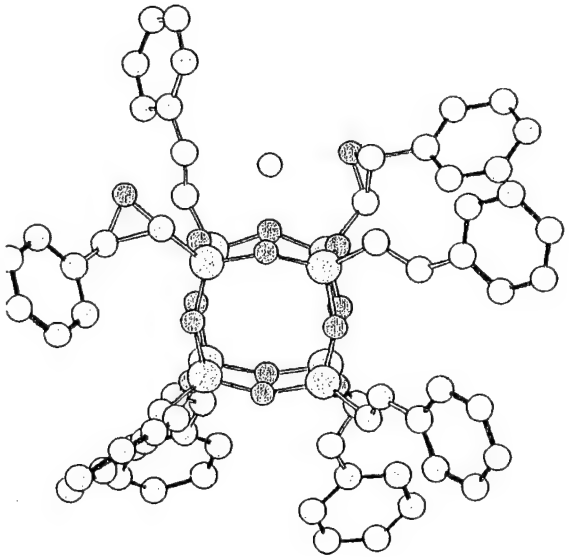


cube diagonal

σ_{Theory} = 322 Å^2

σ_{EXPT} = 324 Å^2

~12%



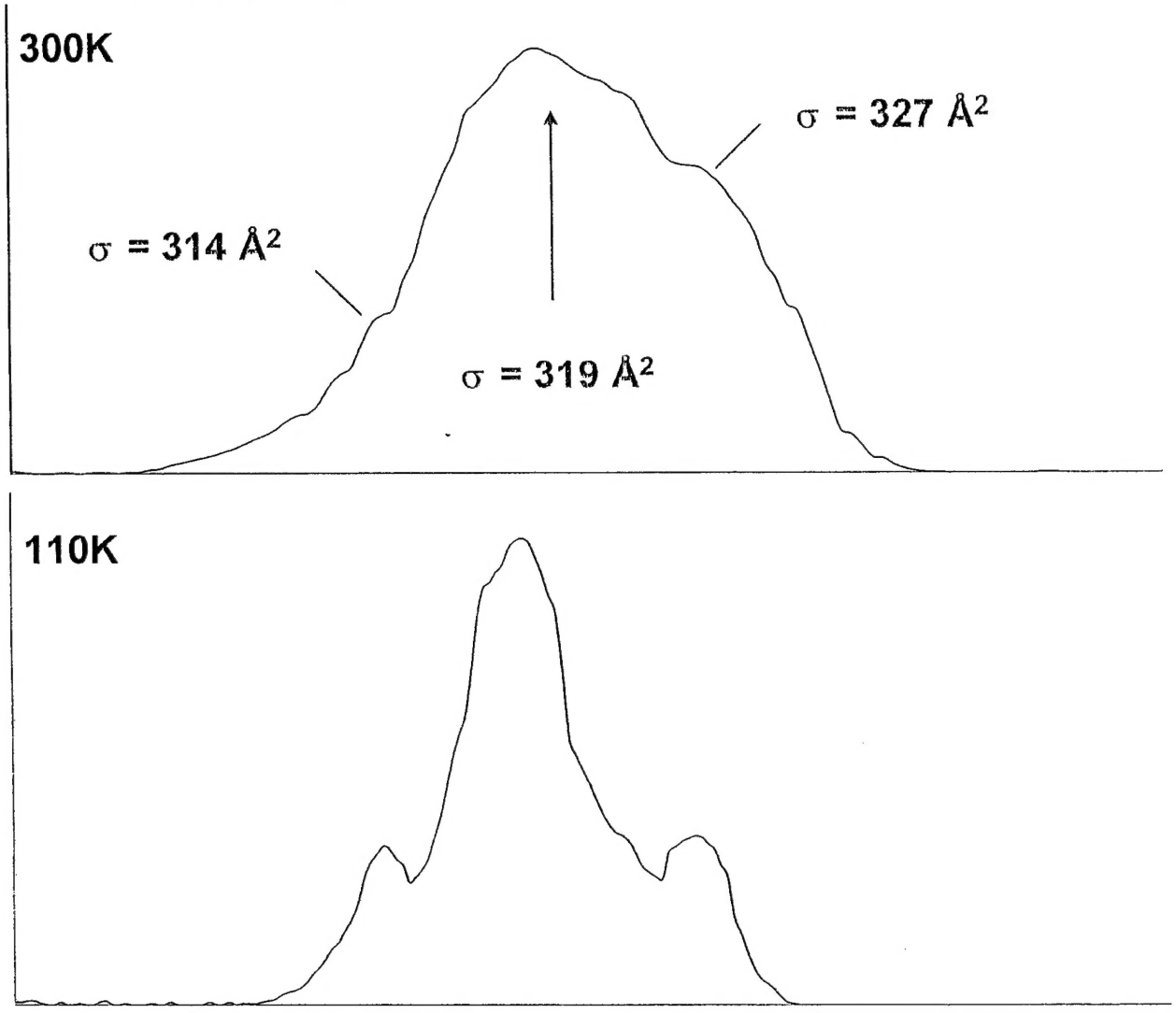
face diagonal

σ_{Theory} = 319 Å^2

σ_{EXPT} = 319 Å^2

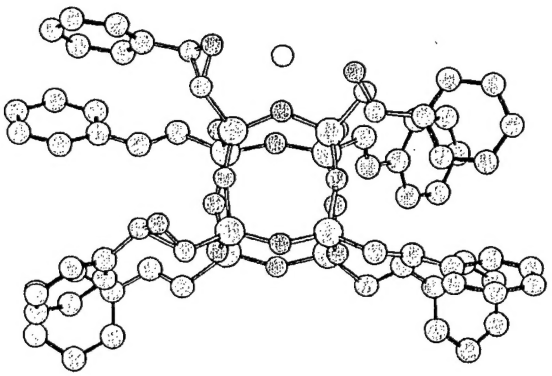
~66%

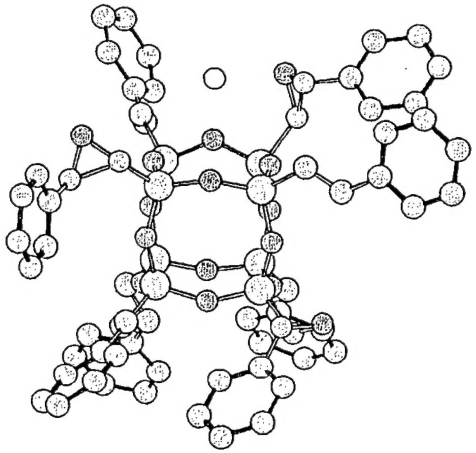
$Na^+Sty_5Ep_3T_8$ ATDs



File name

$Na^+Sty_5Ep_3T_8$ Theoretical Structures





3 on face diagonals

σ_{Theory} = 326 Å^2

σ_{EXPT} = 327 Å^2

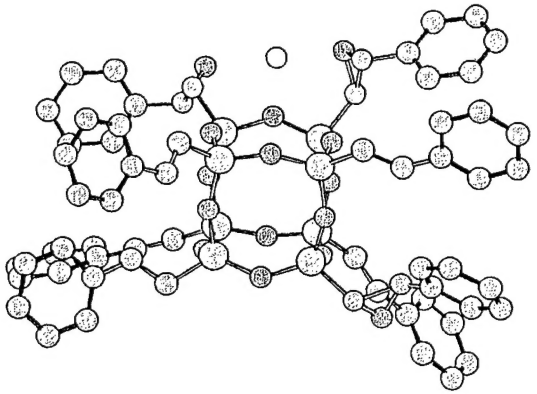
~17%

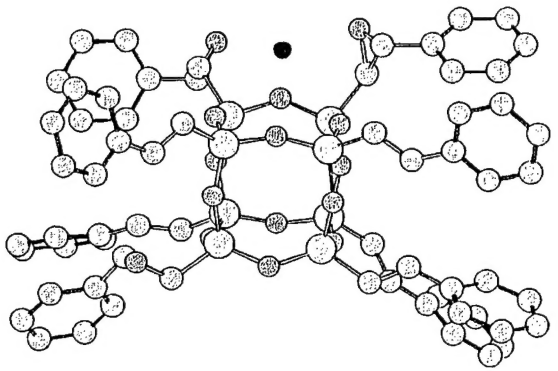
3 epoxides adjacent on face

σ_{Theory} = 314 Å^2

σ_{EXPT} = 314 Å^2

~17%





2 adjacent and 1 on the opposite edge:

σ_{Theory} = 319 Å^2

σ_{EXPT} = 319 Å^2

~66%

Summary for Styrene Epoxy T_8 POSS System

- For a given x, y the distribution of the geometric isomers can be obtained from ion mobility studies
- Can determine x, y distributions of $Sty_xEp_yT_8$ from mass spectrum
- Size of Epoxy intermediate between Sty_8T_8 and $PhenEt_8T_8$
- ***Future Work***: Model Hardening reactions with Monofunctional Amine Reagents

Acknowledgments

Erin Baker

Jennifer Gidden

Paul Kemper

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AFOSR-Michael Berman and Charles Lee